

EFFECT OF THE APPLIED CURRENT DENSITY AND DEPOSITION TIME ON ELECTRO-CODEPOSITION PROCESS OF COBALT MATRIX REINFORCED WITH NANO-CeO₂

This research paper aims to study the influence of some of the main parameters applied to the electrodeposition process on the nanocomposite layers obtained by strengthening the cobalt matrix with cerium oxide nanoparticles. Thus, the current efficiency (process efficiency) and the degree of inclusion of cerium oxide nanoparticles into cobalt matrix are analyzed according to the current density, the concentration of nanoparticles dispersed in the deposition electrolyte and time of the process. The choice of the optimal parameters imposed on the electrodeposition process lead to the improvement of the quality of the obtained layers, to the reduction of production costs and last but not least to the improvement of corrosion and tribocorrosion resistance of the material. The obtained results show an increase of current efficiency in the process of the deposited layers with the increase of time and current density applied. There is also a slight increasing in the current efficiency of the obtained layers with the increase of the concentration of nanoparticles dispersed in the deposition electrolyte. The increase of the current density, time and the concentration of nanoparticles also have an effect on the degree of embedded CeO₂ nanoparticles into cobalt matrix for the studied nanocomposite layers. The degree of inclusion of nanoparticles decreases for the same studied system with the increasing of the current density.

Keyword: Electrochemical deposition; Cobalt matrix; CeO₂ nanoparticles; Current density; Electrolysis time

1. Introduction

The application of coatings is one of the available approaches for improving the surface of materials. Over the years, various coating techniques and materials have been used in order to improve the surface properties of biomaterials. Although nanocomposite materials were initially obtained by the chemical vapor deposition method, the electrodeposition technique has shown a more attractive approach. Electrochemical deposition is one of the most widely used surface improvement techniques, which has seen a significant increase among researchers.

A unique technique in which a variety of materials can be processed, including polymers, metals and even ceramics.

This is demonstrated by the large number of articles in recent years that have as their subject “electrodeposition”. A simple “search” for keywords on the site <http://apps.webofknowledge.com/>, publications per year, it generates a number of 25101 publications in the period 2012-2020 with this topic.

Electrodeposition consists in the deposition on the surface of the substrate of metallic or non-metallic particles of different sizes through an electrolysis process, by chemical changes that

are produced when a current passes to improve the properties of the material [1-2].

The synthesis of composite materials involves an atomic deposition process as well as its precise control. The main advantages that recommend the use of the electrodeposition method for obtaining composite layers are the obtaining of a homogeneous distribution of particles, the reduction of the amount of waste, the low cost of the obtaining equipment and simple operating conditions.

Electrodeposition of metals and alloys is an interesting domain and has a wide range of applicability in various fields. The electrodeposition technique involves the deposition of metals or alloys on a conductive surface by electrolysis of an electrolyte, which can be an aqueous solution, a simple salt or a complex one. The electrochemical cell consists of an anode (positive electrode), a cathode (negative electrode), an electrolyte bath, an electric current source and a voltmeter [3].

The electrodeposition of metal matrix nanocomposite coatings is very complex and requires the optimization of process operating parameters to produce high quality coatings with improved functional properties. Several parameters have been re-

¹ DUNAREA DE JOS UNIVERSITY OF GALATI, FACULTY OF ENGINEERING, COMPETENCES CENTRE: INTERFACES-TRIBOCORROSION-ELECTROCHEMICAL SYSTEMS (CC-ITES), 47 DOMNEASCA STREET, RO-800008 GALATI, ROMANIA

* Corresponding author: lidia.benea@ugal.ro



ported in the literature that are very important in the manufacture of composites, as follows: current density, particle concentration, particle size, electrolyte composition, temperature, deposition time, solution pH and stirring speed [4-6]. Given the advantages of this method, a number of advances have contributed to the use of electrochemical deposition for the manufacture of ceramic nanostructured materials for biomedical applications.

Thus, electrodeposition was used by Benea and his team as a method of coating Ti-6Al-4V surgical alloy substrates with hydroxyapatite in order to improve the corrosion and tribocorrosion performance of the alloy in Fusayama Meyer saliva solution [7-8].

Yang and coworkers [9] study the nucleation and growth of anodic electrodeposited cerium oxide thin film on 316L stainless steel [9]. Benea and his team [10-11] studied the electrodeposition of high molecular weight polyethylene (UHMWPE) in the cobalt matrix on the 304L stainless steel substrate in order to improve the corrosive performance in the Hank biological solution [10-11].

Chen and his team [12] studied the electrodeposition of salicylate dextran on 316L stainless steel to improve the properties of corrosion resistance and hemocompatibility of biomedical applications [12]. Lin and his team [13] studied the synthesis of cobalt and hydroxyapatite by electrodeposition on titanium to improve magnetic resonance imaging [13].

Benea and his collaborators [14] studied the electrodeposition of cobalt and ZrO₂ ceramic particles on 304L stainless steel in order to improve the microhardness and increase the corrosion resistance in the Hank biological solution [14]. Simionescu and collaborators [15-16] evaluated the friction and wear behavior (tribocorrosion) of the Co/nano – CeO₂ nanocomposite layers in the Hank biological solution. Demonstrating that by increasing the content of cerium oxide nanoparticles dispersed in the cobalt deposition electrolyte, the loss of wear volume of the nanocomposite layers proved to be less than that of the pure cobalt layer at all normal forces applied, once again confirming the improvement tribocorrosion performance by adding CeO₂ nanoparticles to the cobalt matrix [15-16].

The aim of this study is to observe the influence of electrochemical parameters (influence of current density and deposition time to obtain Co/CeO₂ nanocomposite layers obtained by electro-codeposition process on their properties (current efficiency and degree of inclusion of nanoparticles). The results of the study showing that these two parameters have a significant influence on the layers obtained in terms of current efficiency and degree

of inclusion of cerium oxide nanoparticles incorporated in the nanocomposite layers.

Over time, the electrodeposition method has led to the development of new biomaterials using nanocomposite thin film coatings on metal implants for use in applications with biomedical potential.

2. Experimental

2.1. Materials

In this study, 304L stainless steel was used as a support layer for electrodeposition, purchased from Direct Line Inox, Bucharest in the form of sheets 1.2 mm thick. The composition of the 304L stainless steel support it can see in TABLE 1.

TABLE 1

The chemical composition of 304L stainless steel used in this study

Stainless steel 304L	Percentage of elements [%]					
	C	Ni	Mn	Cr	Fe	Si
	0.030	8.82	1.02	17.44	71.94	0.75

To initiate the electrodeposition process, the 304L stainless steel sample was cut to dimensions 25 mm × 25 mm × 1.2 mm with an active surface area of 17 mm × 25 mm. The cobalt matrix for electrodeposition was purchased from Goodfellow in the form of plates measuring 50 mm × 50 mm, thickness 2 mm, with a purity of 99.9%.

For the nanocomposite hybrid layers obtained in the cobalt matrix, CeO₂ nanoparticles in the form of nanopowder (CAS no. 1306-38-3), purchased from Sigma Aldrich with average particle size <25 nm, packaged in the form of vials weighing 25 g, were used as dispersed phase.

2.2. Experimental procedures

2.2.1. Preparation of electrolyte used

The schematic representation of preparation of electrolyte used is presented in Fig. 1. All chemical reagents used for this study are of analytical purity purchased from Sigma Aldrich.

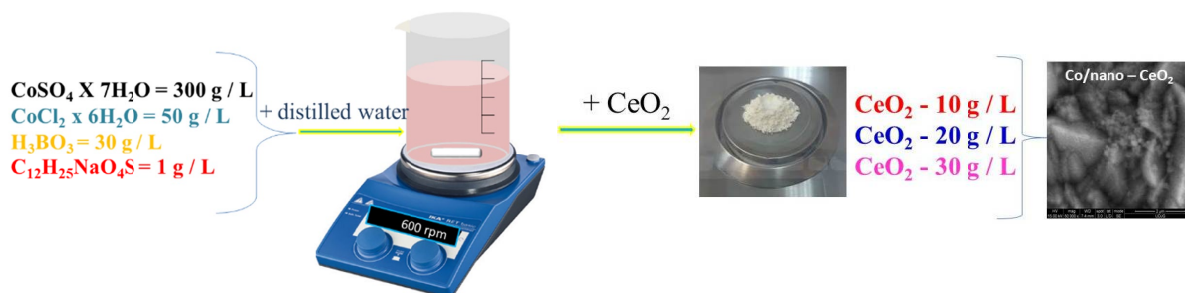


Fig. 1. Schematic presentation of the electrolyte preparation used for electrodeposition of cobalt and electro-codeposition to obtain Co/nano-CeO₂ nanocomposite layers

The characteristics of the electrolyte (pH 4.21, electrical conductivity 36.2 mS/cm² and salinity 22.8 ppt) used for electrodeposition of nano-CeO₂ particles into cobalt metallic matrix, was measured with a Sension⁺ multiparameter.

During the electro-codeposition process, the pH of the electrolyte has been preserved at a pH between 4-4.5 adjusted with hydrochloric acid (HCl 0.1 N) as needed.

2.2.2. Electrochemical cell and the used electrodes

For this study, the electrodeposition cell shown in Fig. 2 is used. The cell is composed of three electrodes respectively (cathode, reference electrode and anode).

To carry out the electrodeposition process, a VoltaLab PGZ 301 electrochemical station was used connected to a laptop whose software runs the Voltmaster4 program.

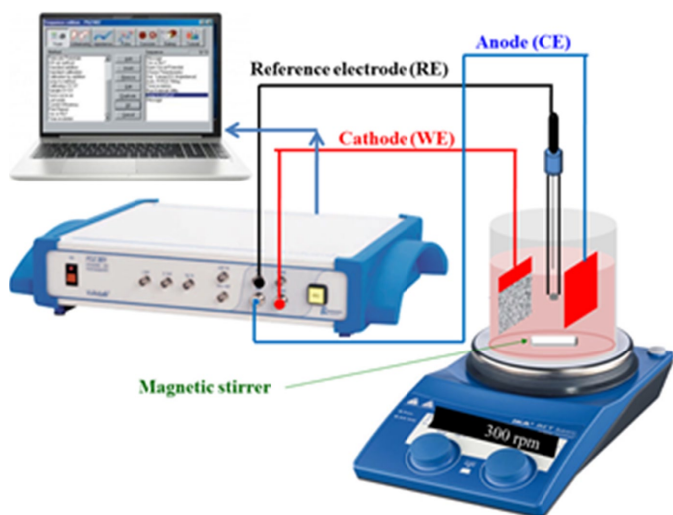


Fig. 2. Schematic draw of the electrochemical cell used in the electrochemical deposition of Co/nano-CeO₂ nanocomposite layers

Working electrode preparation (WE):

A 304L stainless steel plate was used as the working electrode (cathode). The samples were drawn, cut, dotted, drilled, deburred and the electrical contact was made with a copper wire, insulated with epoxy resin to have a well-defined surface of 4.25 cm².

After preparing the cathode, the samples were mechanically cleaned with sanding paper to remove irregularities, chemical degreasing with a solution of NaOH 50 g / L by total immersion of the sample in solution for 10 minutes at a bath temperature of 70°C with the aim of removing grease on the surface of the material, chemical pickling with a solution of HCl 1:1 for 5 min, rinsed with distilled water, then immediately introduced into the electrolyte bath.

Counter electrode preparation (CE):

As an anode, a pure Co plate was used, with electrical contact whose active surface was 9 cm². The pure Co anode

before being immersed in the solution, was degreased with alcohol, rinsed with distilled water, dried in an oven, and after each measurement the cobalt anode was cleaned with 1:1 hydrochloric acid for 2 min.

Reference electrode (RE):

Ag/AgCl (with saturated KCl solution), E = +199 mV vs. NHE at 22°C.

Electrolysis cell:

The electrochemical cell used for electrodeposition process consists of three electrodes. The volume of the electrolyte used for electrodeposition was 160 mL. The dispersion of the nano-particles was done using an electromagnetic stirring system, and the optimum magnetic stirring was established at 300 rotations per minute to have a homogeneous dispersion of nanoparticles into electrolyte.

Working parameters:

The pH of the electrolyte was maintained at 4.21 adjusted with HCl, measured before, during the process and after the electrodeposition process. Deposition were made at room temperature 22 ± 1°C.

Electrochemical measurements:

Chronopotentiometry curves in the absence of CeO₂ nanoparticles in the current density range 23 mA/cm², 48 mA/cm², 72 mA/cm² with a duration of 30 min, 60 min and 90 min, noted in this paper as of pure Co;

Chronopotentiometry curves in the presence of CeO₂ nanoparticles (nanoparticles whose amount present in the cobalt electrolyte is 10 g/L marked Co/nano-CeO₂ – 10 g/L, 20 g/L (Co/nano-CeO₂ – 20 g/L) and 30 g/L (Co / nano-CeO₂ – 30 g/L) in the current density range 23 mA/cm², 48 mA/cm², 72 mA/cm² with a duration of 30 min, 60 min and 90 min.

3. Results and discussion

3.1. The influence of electrodeposition time

3.1.1. The influence of electrodeposition time on the current efficiency (η [%])

The current efficiency was calculated according to Faraday's law as can be seen in the equation below:

$$\eta = \frac{m_p}{m_t} \cdot 100 \text{ [%]} \quad (1)$$

Where: η is current efficiency, m_p – the weight practically electrodeposited, m_t – the weight theoretical electrodeposited calculated according to Faraday's laws.

In Fig. 3. the influence of time (30, 60, 90 min) on the current efficiency for Co/nano-CeO₂ nanocomposite layers with different concentrations of CeO₂ nanoparticles (10, 20,

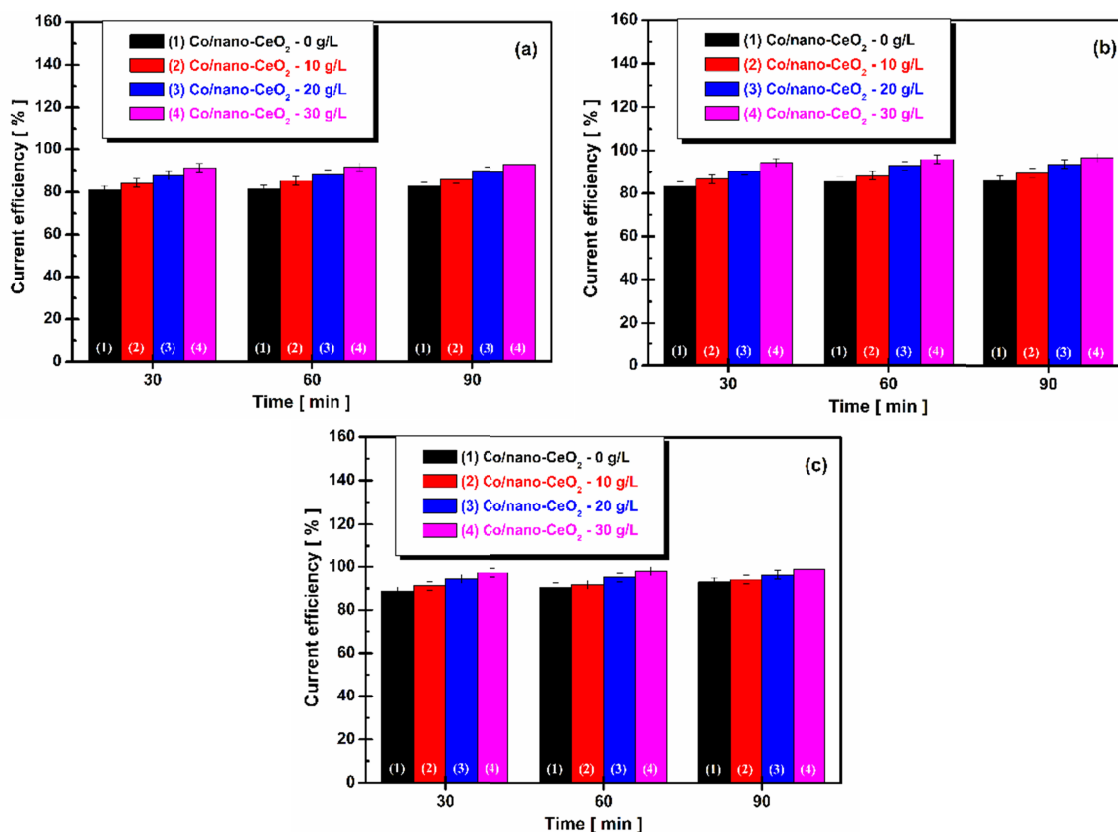


Fig. 3. Current efficiency versus time of electrodeposition for: (1) Co/nano-CeO₂ - 0 g/L; (2) Co/nano-CeO₂ - 10 g/L; (3) Co/nano-CeO₂ - 20 g/L and (4) Co/nano-CeO₂ - 30 g/L at different applied current densities of: (a) 23 mA/cm², (b) 48 mA/cm² and (c) 72 mA/cm²

30 g/L) is compared to the layers obtained without the addition of nanoparticles (pure Co) at different current densities (23, 48, 72 mA/cm²).

Fig. 3a shows that for the pure Co layer at the deposition time of 30 minutes and the current density of 23 mA/cm², the current efficiency has the lowest value starting from 80.91%. This value increases with increasing of deposition time, reaching a current efficiency value of 82.69% at 90 min. The current efficiency for the Co/nano-CeO₂ layer - 10 g/L at the same time (30 min.) is higher, having a value of 84.33% with an increasing tendency with deposition time, reaching at the deposition time of 90 min a value of 86.10%, which is higher as compared with pure cobalt layer.

By increasing the concentration of CeO₂ nanoparticles in the electrodeposition solution, the value of current efficiency increases to a value of 87.65% for the Co/nano-CeO₂ layer - 20 g/L at 30 min time of deposition, reaching a value of 89.52% at the 90 min time of deposition.

In the case of Co/nano-CeO₂ layers - 30 g/L at the time of 30 minutes, the current efficiency starts from a value of 91.16%; this value also increases with the deposition time reaching at the end of the 90 minutes a value of 93.31%.

With the increase of the current density to 48 mA/cm², keeping the same deposition time of 30, 60, 90 min. (Fig. 3b) there is also observed an increase in current efficiency with the increase of the deposition time for all the studied systems. For the pure Co layer it is observed that at the time of 30 min the

current efficiency reaches a value of 83.40%, while this value increases with time to 85.58% for the deposition time of 60 min increasing even more reaching the value of 86.09% at 90 minutes of deposition time.

For the Co/nano-CeO₂ layer - 10 g/L the current efficiency value increases at 30 minutes to 86.67% compared to the pure Co layer at the same time of deposition and increases to 88.31% for the time of 60 minutes, reaching a value of 89.35% for the time of 90 minutes.

As the concentration of nanoparticles increases, there is a tendency to increase the values of the current efficiency with the deposition time.

For the Co/nano-CeO₂ layer with the addition of 20 g/L CeO₂ nanoparticles, at 30 minutes, the current efficiency has a value of 90.49%, which increases at 92.94%, for 60 minutes of deposition time. By increasing the deposition time at 90 min, the current efficiency increases even more at 93.22%. Fig. 3c shows the variation of the current efficiency as a function of the deposition time (30 minutes, 60 minutes, 90 minutes) for the functional layers obtained at the current density of 72 mA/cm².

From the Fig. 3c it is observed that for the pure Co layers the value of the current efficiency stops at at 92.97%, for 90 min deposition time while for the nanocomposite layers the values exceed 91% for all the studied nanoparticle concentrations. The current efficiency values increase with deposition time reaching for Co/nano-CeO₂ layers with the addition of CeO₂-30 g/L at 90 minutes the value of 98.90%.

From Fig. 3 it can be concluded that the current efficiency increases with the deposition time for all the studied systems, at the same time the current efficiency is increasing slightly for the hybrid nanocomposite layers as compared to the pure Co layer at the same deposition time and the same applied current density.

It is also noticed that for the layers obtained without the addition of nanoparticles (pure Co) the current efficiency starts from a value of 80.91% and does not exceed the value of 92.97%. The current efficiency values for nanocomposite layers are higher. This trend of increasing the current efficiency with the increase of the deposition time has been reported in the literature also by other authors [17-19].

3.1.2. The influence of electrodeposition time on the inclusion degree of CeO₂ nanoparticles into cobalt matrix

The degree of inclusion of cerium oxide nanoparticles was calculated from the SEM-EDX elemental analysis, depending on the three deposition times (30, 60, 90 minutes) at current densities of 23, 48, 72 mA/cm². Data for EDX analysis were collected from the entire sample scanning area in order to determine the percentage of inclusion of the element Ce into the cobalt matrix. The percentage of incorporation of CeO₂ nanoparticles into the Co matrix was determined by transforming the mass percentage Ce (wt.%) from the molecular weight of CeO₂. The molar mass of the element Ce has a value of 140.116 g/mol. The mass

percentage for the element Ce included in the cobalt matrix according to the EDX analysis, is shown in Fig 4a,b,c for the times 30 min, 60 min and 90 min at current densities of 23 mA/cm², 48 mA/cm² and 72 mA/cm².

Given the diagrams exemplified in Fig. 4, it can be said that the degree of CeO₂ nanoparticles inclusion into the cobalt matrix increases with increasing time of deposition for all studied systems and with increasing the concentration of nanoparticles in the electrodeposition electrolyte.

From Fig. 4a, it is observed that for addition of 10 g/L CeO₂ nanoparticles within 30 min of deposition the degree of inclusion of CeO₂ nanoparticles in the nanocomposite layer has a value of 2.32%, a value of 2.62% at 60 minutes and reaches a percentage of 6.81% at 90 minutes of deposition time.

With the increase of the concentration of CeO₂ nanoparticles to 20 g/L, an increase of the inclusion percentage of the studied nanoparticles was observed as compared to the Co/nano-CeO₂ system – 10 g/L at the same time studied. Therefore, for the Co/nano-CeO₂ system – 20 g/L, at the time of 30 minutes, the percentage of inclusion of the studied nanoparticles into the cobalt matrix is 4.86% while at the time of 60 min. the percentage is 6.95%, reaching a value of 15.0%. at deposition time of 90 minutes. For the Co/nano-CeO₂ system – 30 g/L there is an increase in the percentage of inclusion of nanoparticles as compared to systems in which CeO₂ was added in a concentration of 10 g/L and 20 g/L. At the lowest time studied it is observed that for the Co/nano-CeO₂ system – 30 g/L the percentage of inclusion of nanoparticles has a value of 10.2%, this percent-

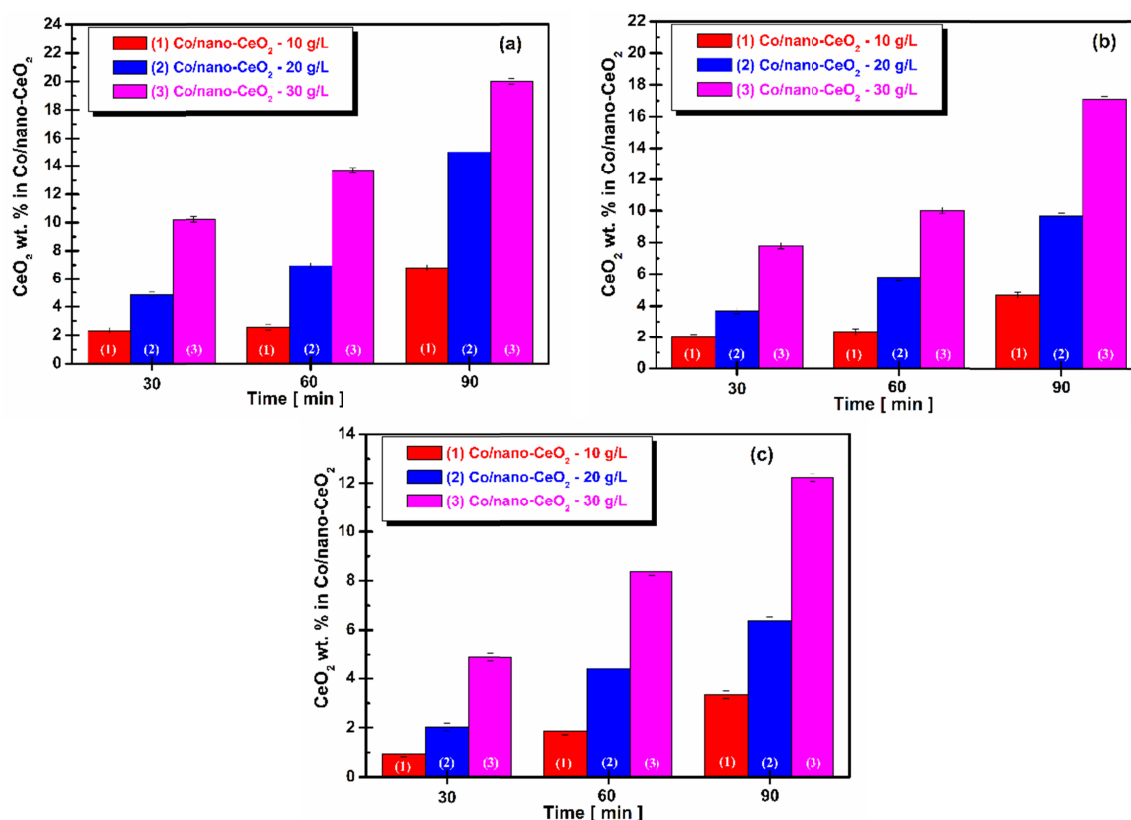


Fig. 4. The influence of time on the degree of inclusion of CeO₂ nanoparticles into the cobalt matrix for: (1) Co/nano-CeO₂ – 10 g/L, (2) Co/nano-CeO₂ – 20 g/L and (3) Co/nano-CeO₂ – 30 g/L at current densities of (a) 23 mA/cm², (b) 48 mA/cm² and (c) 72 mA/cm²

age increases with increasing time reaching at the highest time studied at a value of 20.0%. In Fig. 4b and 4c the same trend is observed. The same trend of increasing the degree of inclusion of nanoparticles into different metal matrices with increasing deposition time and increasing the concentration of nanoparticles in the electrolyte is observed by other authors [17-18].

3.2. The influence of current density on the electrodeposition process

3.2.1. The influence of current density on the current efficiency (η [%])

The influence of current density (23 mA/cm², 48 mA/cm² and 72 mA/cm²) applied to the electrodeposition process to obtain cobalt pure and nanocomposite layers at different deposition time is shown in Fig. 5(a, b, c).

From Fig. 5a at the 30 min time of deposition, it is observed that in the current density domain between 23-72 mA/cm², the current efficiency for nanocomposite layers is higher, reaching up to a percentage of 97.33% for the Co/nano-CeO₂ system – 30 g/L at the highest current density, as compared to the pure Co layer whose percentage of current efficiency is 87% at the same current density. Fig. 5b shows a higher current efficiency for the same current densities but at a electrodeposition time of 60 minutes.

Thus, for the pure Co layer, the current efficiency have a constant value of 90.61% at a current density of 72 mA/cm², and

for the nanocomposite layer obtained with an addition of 30 g/L of nanoparticles, the current efficiency at the same current density is 98.05%. For the same current densities but at a deposition time of 90 minutes (Fig 5c) the current efficiency value obtained for the pure Co layer at the current density of 72 mA/cm² reaches 92.97% while for the same current density value for Co/nano-CeO₂ – 30 g/L reaches a value of 98.90%. Similar results trend in terms of increasing current efficiency with increasing current density have been reported by other authors [19-20].

3.2.2. The influence of current density on the degree of inclusion of CeO₂ nanoparticles into cobalt matrix

The methodology to calculate the degree of inclusion of cerium oxide nanoparticles into cobalt matrix, for the graphs presented in Fig. 6 is the same as the one summarized in subchapter 3.1.2.

As it can be seen in Fig. 6a, the degree of inclusion of nanoparticles decreases with increasing current density for all systems studied. In instance, for the nanocomposite layer with addition of 10 g/L nano CeO₂ in electrolyte, it was observed that at the current density of 23 mA/cm², the degree of inclusion of the nanoparticles reaches a percentage of 2.32%, also for the same system studied but at the current density of 48 mA/cm² the value decreases to a percentage of 1.99%, and for 72 mA/cm² the value decreases even more to a percentage of 0.93%. It is also observed from Fig. 6a that the value of the inclusion percentage

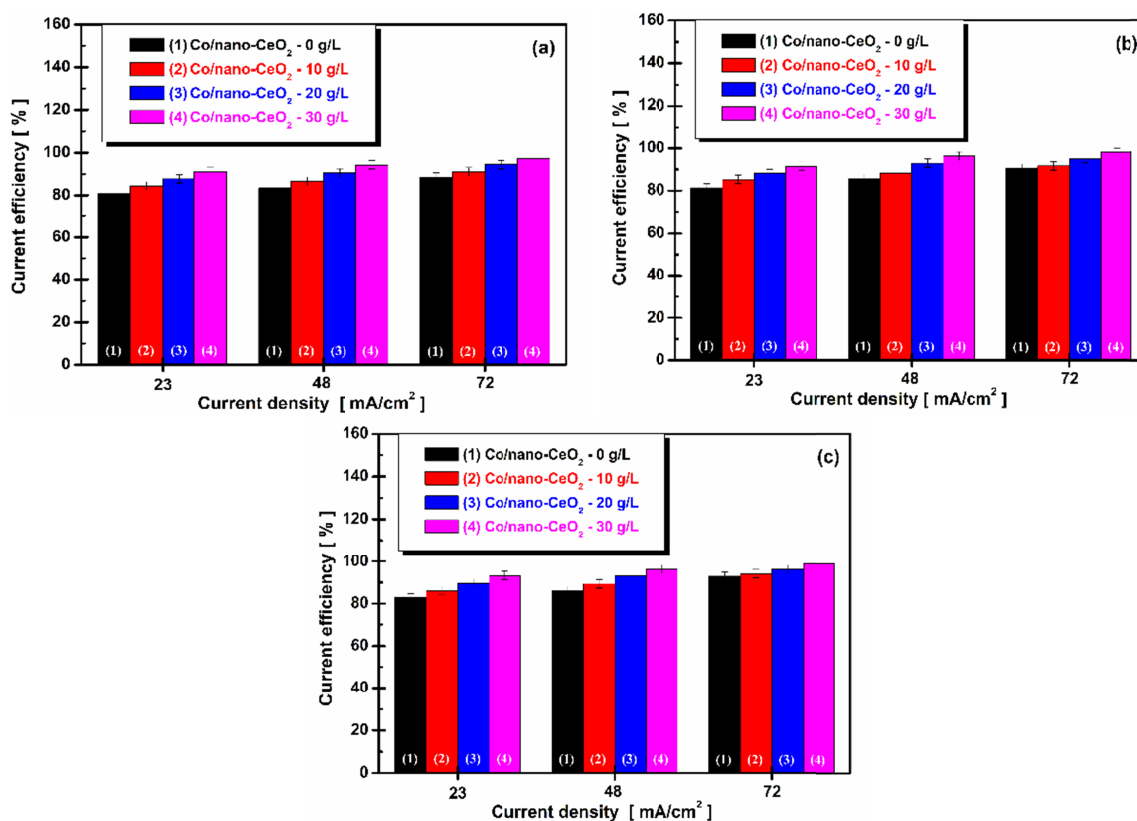


Fig. 5. The influence of current density on the current efficiency for: (1) Co/nano-CeO₂ – 0 g/L; (2) Co/nano-CeO₂ – 10 g/L; (3) Co/nano-CeO₂ – 20 g/L și (4) Co/nano-CeO₂ – 30 g/L at deposition time: (a) 30 min, (b) 60 min and (c) 90 min

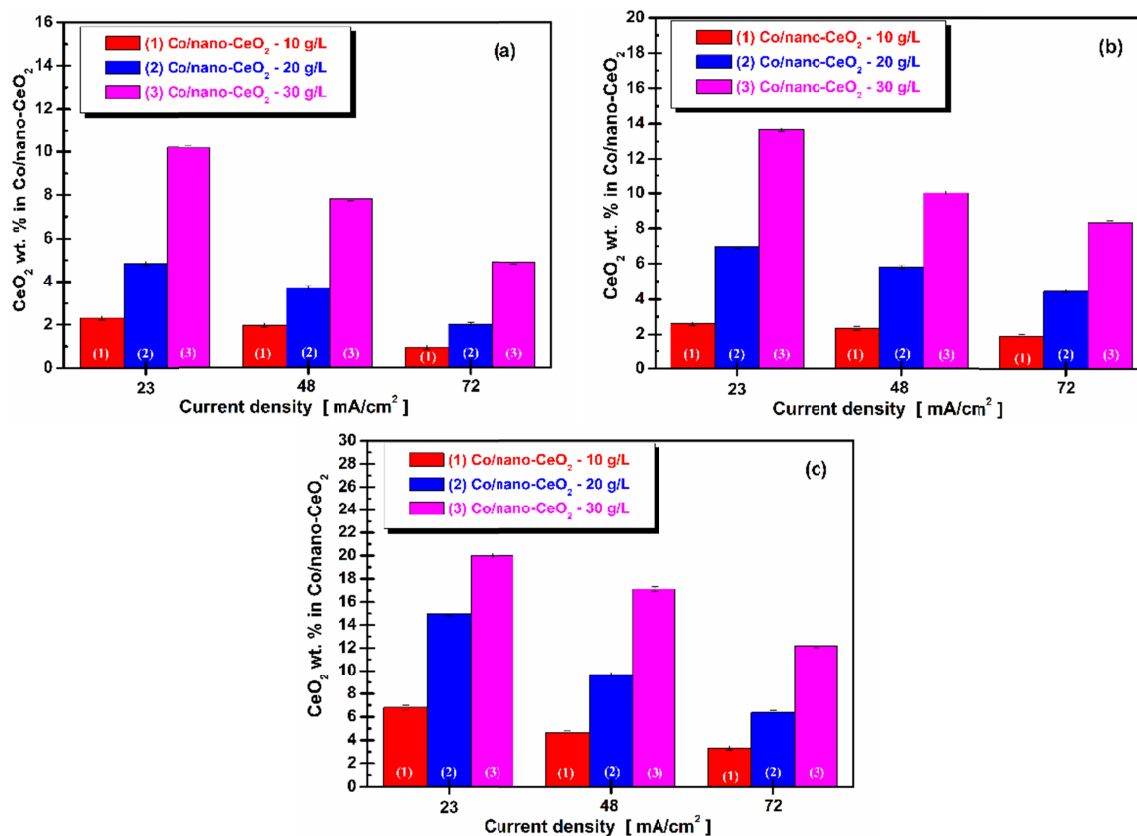


Fig. 6. The influence of current density on the degree of inclusion of CeO₂ nanoparticles into the cobalt matrix for: (1) Co/nano-CeO₂ – 10 g/L, (2) Co/nano-CeO₂ – 20 g/L and (3) Co/nano-CeO₂ – 30 g/L at time: (a) 30 min, (b) 60 min and (c) 90 min

of CeO₂ nanoparticles increases with increasing concentration of nanoparticles for the same current density. The same trend of decreasing the degree of inclusion of nanoparticles with increasing current density is observed in Figs 6b and 6c. Other authors have also reported that the degree of inclusion of nanoparticles decreases with increasing the current density; this behavior is possible because the current density has a considerable effect on the current-potential relationship in any electrodeposition process [21-24].

4. Conclusions

In conclusion, parameters such as current density, electrolyte concentration, and electrodeposition time play very important roles in electrodeposition quality performance. Therefore, in order to obtain high quality of the electrodeposition layer some parameters such as current density and time must be studied accordingly.

After the electrodeposition process can be conclude that with the increase of the current density and time of deposition, an increase of the current efficiency was observed.

For the pure Co layers at all the applied current densities and duration of electrolysis studied the current efficiency show lower values (but over 80%) as compared to the obtained Co/CeO₂ nanocomposite layers in which different concentrations of nanoparticles were added.

The highest current efficiency (99%) is obtained for electro-codeposition of Co/nano-CeO₂ system with 30 g L CeO₂ nanoparticles added to cobalt electrolyte.

By analysis the degree of inclusion of nanoparticles, it was observed that with the increase of the deposition time and the concentration of CeO₂ nanoparticles added in the electrolyte the degree of inclusion of nanoparticles into the nanocomposite layer increases.

The degree of inclusion of nanoparticles into cobalt matrix decreases for the same system studied with increasing of current density.

These results are comparable with data from the literature obtained by other authors who studied composite systems.

This research confirms the importance of studying and choosing optimal parameters, such as current density and time, to obtain nanocomposite layers with high current efficiency and with a controlled amount of dispersed phase included in the metal matrix in order to increase the lifetime of materials for various applications.

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REFERENCES

- [1] Y.D. Gamburg, G. Zangari, G. Theory and Practice of Metal Electrodeposition, (2011).
DOI: <https://doi.org/10.1007/978-1-4419-9669-5>
- [2] F. Nasirpour, Electrodeposition of Nanostructured Materials, Springer Series in Surface Sciences, (2017).
DOI: <https://doi.org/10.1007/978-3-319-44920-3>
- [3] L. Benea, Metode avansate de investigare a materialelor, Galați: Academica, (2017). ISBN 978-606-606-003-5
- [4] N. Malatji, P.A.I. Popoola, Tribological and Corrosion Performance of Electrodeposited Nickel Composite Coatings, Electrodeposition of Composite Materials, (2015).
DOI: <http://dx.doi.org/10.5772/62170>
- [5] F.C. Walsh, C. Ponce de Leon, Transactions of the IMF. **92** (2), 83-98 (2014).
- [6] E.S. Güler, Effects of Electroplating Characteristics on the Coating Properties, Electrodeposition of Composite Materials, (2016).
- [7] L. Benea, E. Mardare-Danaila, M. Mardare, J.P. Celis, Corros. Sci. **80**, 331-338 (2014).
- [8] L. Benea, E. Mardare-Danaila, J.P. Celis, Tribol. Int. **78**, 168-175 (2014).
- [9] Y. Yang, Int. J. Electrochem. Sci. **12**, 5304-5319 (2017).
- [10] L. Benea, E. Dănăilă, Key Eng. Mater. **699**, 57-62 (2016).
- [11] L. Benea, M. Mardare-Prlea, Dig. J. Nanomater. Biostructures. **6** (3), 1025-1034 (2011).
- [12] B. Chen, J. Chen, L. Yang, G. Zhao, G. Ding, Surf. Eng. **30** (10), 763-767 (2014).
- [13] W.C. Lin, C.C. Chuang, P.T. Wang, C.M. Tang, Materials **12** (1), 116 (2019).
- [14] L. Benea, P. Ponthiaux, F. Wenger, Surf. Coat. Technol. **205** (23-24), 5379-5386 (2011).
- [15] N. Simionescu, L. Benea, J.P. Celis, IOP Conf. Ser. Mater. Sci. Eng. **572**, 012003 (2019).
- [16] N. Simionescu, L. Benea, J.P. Celis, J. Mech. Behav. Biomed. Mater. **101**, 103443 (2020).
- [17] F.S. Sorcaru, PhD thesis, Suprafete functionale Co/nano-ZrO₂ obtinute prin electrodepunere pentru utilizarea in industrie și biomedicina, Dunarea de Jos University, Galati (2012).
- [18] I.A. Pavlov, PhD thesis, Influenta tratamentelor electrochimice a suprafetelor (straturi nanocompozite in matrice de nichel) asupra rezistentei la coroziune și uzura, Dunarea de Jos University, Galati (2012).
- [19] L. Benea, J.P. Celis, Materials **9** (4), 269 (2016).
- [20] O.E. Kongstein, G.M. Haarberg, J. Thonstad, J. Appl. Electrochem. **37** (6), 669-674 (2007)
- [21] S. Kuo, J. Chin. Inst. Eng. **27** (2), 243-251 (2004).
- [22] E. Beltowska-Lehman, P. Indyka, A. Bigos, M.J. Szczerba, J. Guspiel, H. Koscielny, M. Kot, Mater. Chem. Phys. **173**, 524-533 (2016).
- [23] X. Xia, I. Zhitomirsky, J.R. McDermid, J. Mater. Process. Technol. **209** (5), 2632-2640 (2009).
- [24] H.Y. Zheng, M.Z. An, J. Alloys Compd. **459** (1-2), 548-552 (2008).